Supporting Information

Marked Indolyl *vs* Indolinyl-Substituent Effects on Solid-State Structure, Carrier Mobility and Photovoltaic Efficiency of Asymmetrical Squaraine Dyes

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Contents

Table S1. Summary of crystal data, data collection, and refinement parameters for **1a** and **1b**.

Compound	**1a**	**1b**
Empirical formula	$C_{40}H_{38}N_2O_4$	$C_{40}H_{36}N_2O_4$
Formula weight	610.72	608.71
Temperature	140.15 K	143.05 K
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$
a/Å	13.6013(7)	7.41851(17)
b/Å	15.3860(6)	40.3306(11)
c/Å	15.6472(9)	11.5514(3)
α/°	90.00	90.00
β/°	109.803(4)	99.732(2)
γ/°	90.00	90.00
Volume/Å^3	3080.8(3)	3406.36(15)
Z	4	4
ρ_{calc}mg/mm^3	1.317	1.187
m/mm^{-1}	0.673	0.077
F(000)	1296.0	1288.0
Crystal size/mm^3	0.08 × 0.04 × 0.03	0.4 × 0.35 × 0.3
2θ range for data collection	7.462 to 139.114°	5.926 to 52.744°
Index ranges	$-15 \le h \le 16$, $-18 \le k \le 18$, $-18 \le l \le 18$	$-9 \le h \le 9$, $-32 \le k \le 50$, $-14 \le l \le 13$
Reflections collected	19712	26126
Independent reflections	5575 [R(int) = 0.1046]	6964 [R(int) = 0.0429]
Data/restraints/parameters	5575/340/498	6964/0/431
Goodness-of-fit on F^2	1.020	1.061
Final *R* indexes [I>=2σ (I)]	R_1 = 0.0777, wR_2 = 0.2034	R_1 = 0.0561, wR_2 = 0.1460
Final *R* indexes [all data]	R_1 = 0.1119, wR_2 = 0.2364	R_1 = 0.0666, wR_2 = 0.1524
Largest diff. peak/hole / e Å^{-3}	0.30/-0.27	0.25/-0.22

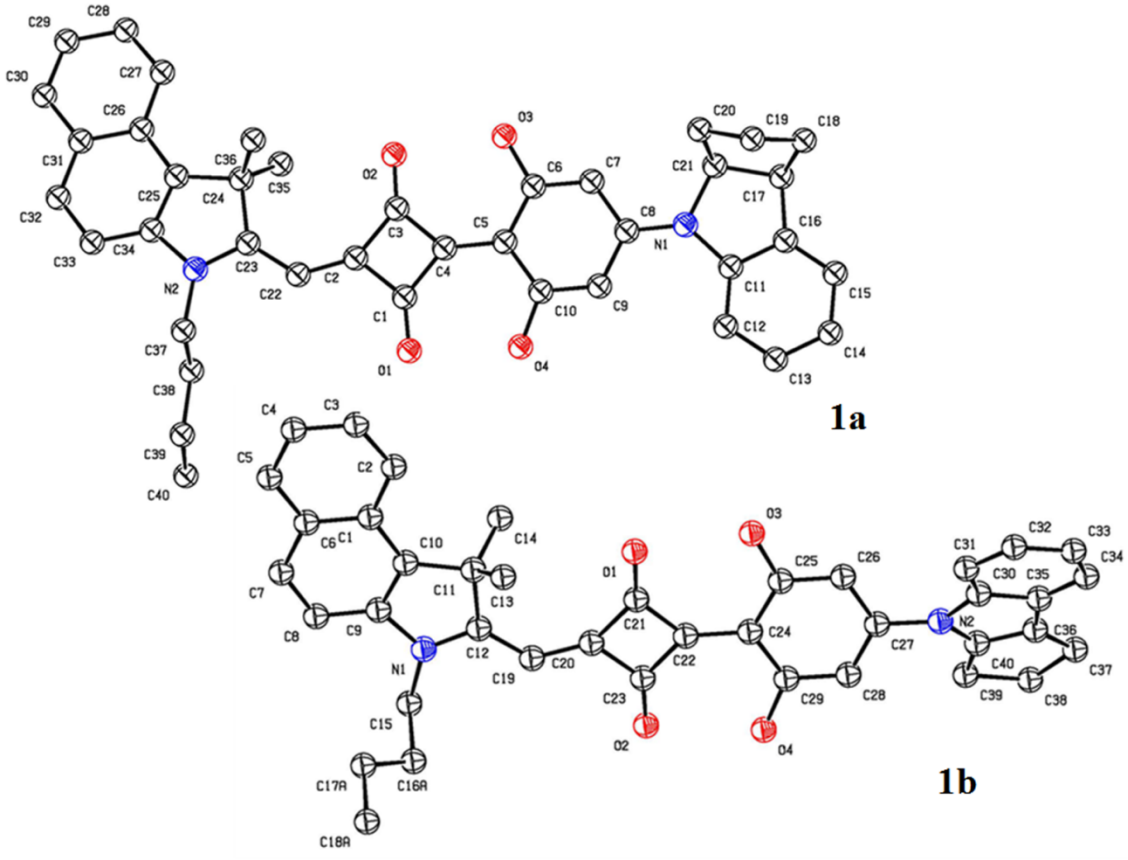

Figure S1. ORTEP drawing (hydrogen atoms removed for clarity, C=blank, N=blue, O=red) of compounds **1a** and **1b**.

Table S2. Comparison of calculated geometries of **1a** and **1b** with experimental data from X-ray crystal analysis[a)]

Bond lengths	Experimental	Calculated [b)]	Bond/Torsion angles	Experimental	Calculated [b)]
1a					
C37-N2	1.465(4)	1.475	C36-C24-C35	112.5(3)	111.99
N2-C23	1.345(4)	1.366	C23-C22-C2	132.5(3)	132.65
C23-C22	1.386(5)	1.402	C8-N1-C21	120.7(3)	121.56
C22-C2	1.384(4)	1.386	C8-N1-C11	131.6(3)	127.95
C2-C1	1.463(4)	1.474	C11-N1-C21	106.9(3)	110.48
C1-C4	1.458(4)	1.461	C21-C20-C19	104.4(4)	104.62
C4-C3	1.450(4)	1.464	C19-C18-C17	104.1(5)	104.80
C3-C2	1.478(4)	1.481	C4-C5-C6	122.8(3)	122.18
C3-O2	1.244(4)	1.273	C23-C22-C2-C3	5.0(9)	-0.75
C1-O1	1.241(4)	1.270	C3-C4-C5-C6	0.5(6)	0.17
C4-C5	1.419(4)	1.414	C1-C4-C5-C10	0.0(6)	-0.73
C8-N1	1.376(4)	1.389	C9-C8-N1-C11	4.1(6)	27.02
N1-C11	1.428(4)	1.416	C7-C8-N1-C21	-6.2(6)	24.29
N1-C21	1.518(4)	1.506	C8-N1-C21-C20	78.2(4)	60.55
1b					
C15-N1	1.470(2)	1.481	C13-C11-C14	113.93(15)	112.09
N1-C12	1.341(2)	1.360	C12-C19-C20	131.40(17)	132.49
C12-C19	1.408(2)	1.408	C27-N2-C30	127.60(15)	127.03
C19-C20	1.374(3)	1.379	C27-N2-C40	125.64(16)	126.01
C20-C23	1.472(2)	1.479	C30-N2-C40	106.69(15)	106.94
C23-C22	1.448(3)	1.457	C40-C39-C38	101.54(15)	101.09
C22-C21	1.449(2)	1.458	C38-C37-C36	102.64(15)	102.19
C21-C20	1.490(3)	1.487	C22-C24-C25	122.44(15)	121.88
C21-O1	1.241(2)	1.271	C12-C19-C20-C21	3.6(4)	1.18
C23-O2	1.238(2)	1.268	C21-C22-C24-C25	-5.1(3)	0.25
C22-C24	1.433(2)	1.424	C28-C27-N2-C40	36.0(2)	40.66
C27-N2	1.411(2)	1.414	C27-N2-C40-C39	-0.4(3)	-0.15
N2-C30	1.401(2)	1.420	C26-C27-N2-C30	33.7(2)	39.78
N2-C40	1.397(2)	1.405	C23-C22-C24-C29	-3.8(3)	0.40

[a)] The bond lengths are in angstroms and the angles are in degrees; [b)] Calculated in acetonitrile.

The optimized structures for both compounds have been calculated at B3LYP/6-31G(d) level in acetonitrile. Because the experimental data were obtained in condensed solid phase, yet the computational values derived from liquid phase that are free of stacking effects, compared with the experimental data, some of the optimized torsion angles are slightly larger than the corresponding experimental values.

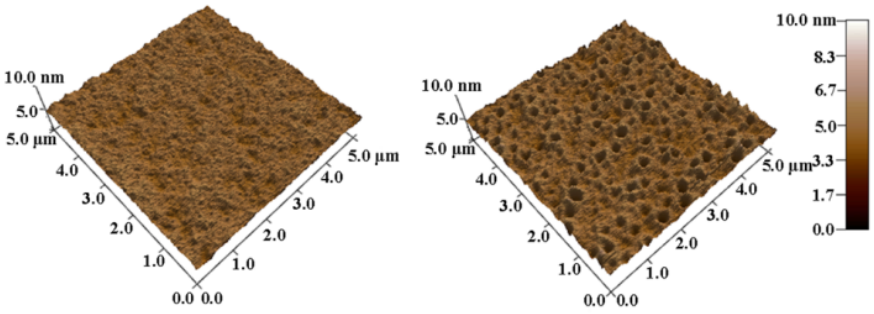

Figure S2. 3D images obtained by tapping-mode AFM of ASQ:$PC_{71}BM$ (1:8, w/w) composite films. Left: **1a**, Right: **1b**.